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Equilibrium and Kinetic Studies of Biosorption of Zn(II) Ions from Wastewater Using Modified Corn Cob

Achanai Buasri[a,b,]*, Nattawut Chaiyut[a,b], Kessarin Tapang[a], Supparoek Jaroensin[a], Sutheera Panphrom[a]

[a]*Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand*

[b]*National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand*

Abstract

The objective of this study was to convert corn cob to heavy metal ion biosorbent for wastewater treatment. Corn cob was modified with phosphoric acid (PA) to help improve their natural biosorption capacity. The influence of various parameters such as initial solution concentration, initial biomass concentration and temperature on biosorption potential of agricultural waste material was studied in detail. The adsorption equilibrium data were adequately characterized by Langmuir, Freundlich and Temkin equations. The equilibrium biosorption isotherms showed that modified corn cob possess high affinity, with sorption capacities of 79.21 mg Zn(II) per 1 g biomass. Analysis indicated that pseudo-second-order kinetics controlled the adsorption rate. All results showed that corn cob is an alternative low cost biosorbent for removal of heavy metal ions from aqueous media.

Keywords: Equilibrium, Kinetic, Biosorption, Wastewater, Modified Corn Cob

1. Introduction

Industrial wastewater contaminated with heavy metals is commonly produced from many kinds of

* Corresponding author. Tel.: +66-34-219-363; fax: +66-34-219-363.
E-mail address: achanai130@gmail.com.

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industrial processes. Therefore, if this wastewater is not treated with a suitable process or leaked from storage tanks, it can cause a serious environmental problem in the natural eco-system [1]. Whenever toxic heavy metals are exposed to the natural eco-system, accumulation of metal ions such as zinc, copper and lead in human body will be occurred through either direct intake or food chains [2]. Therefore, heavy metal should be prevented before it reaches to the natural environments because of its toxicity. Several methods have been employed to remove heavy metal ions from wastewater, which include precipitation, oxidation/reduction, flotation, reverse osmosis, ion exchange, ultra filtration, electrochemical technique and biological process [3]-[7]. Adsorption is the most attractive method due to its simplicity, convenience and high removal efficiency [8],[9]. Agricultural by-products have been reported as having natural ion-exchange capability [10]. Some of these by-products include soybean hulls, peanut hulls and corn cobs, which have several advantages over commercial resins in that they are less expensive, biodegradable and come from renewable resources. Modification of agricultural by-products could enhance their natural ion-exchange capability and add value to the by-products [11].

Corn is one of the largest production crops in the world. Corn cob, corn husk, corn leaf and corn stalk are abundant agriculture residues form corn, but most are burnt without utilization [12]. In this study, we treated corn cobs with phosphoric acid (PA) to modify the biosorbents and analyzed their property. The biosorption capacity of the modified corn cob to remove zinc(II) from wastewater as a function of initial solution concentration, initial biomass concentration and temperature. The adsorption equilibrium was expressed using Langmuir, Freundlich and Temkin models. Furthermore, two adsorption kinetic models were calculated to analyze the experimental data.

2. Experimental

2.1. Biosorbent and metal solution preparation

Reaction of corn cob with PA was performed according to the method described in the previous research [13]. In a 500 mL, three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer, and a stirrer, 224 g urea was added, heated at 140 ^oC and flushed with nitrogen. 30 g corn cob and 168 mL PA were added alternatively portionwise to the molten urea in order to reduce the foaming. The reaction was allowed to proceed at 150 ^oC for 2 h. The adsorbent was washed with distilled water and acetone. A sample was treated with 0.5 M hydrochloric acid for 24 h under slow stirring. The modified corn cob was washed several times with deionized water to remove excess acid from biosorbent. It was dried for 24 h at 60 ^oC in an oven before starting the experiments.

All chemicals used were analytical grade reagents (Merck, >99 %purity). Stock solutions of metals were prepared in a concentration of 2,000 ppm using nitrate salts dissolved in deionized water with a resistivity value of 17 MΩ. The chemicals used in the batch experiments were nitrate solutions of $Zn(NO_3)_2$.

2.2. Equilibrium and kinetic experiments

The batch mode adsorption isotherm was carried out at 30-70 ^oC. Amount of 1.0-5.0 g modified corn cob were introduced into conical flasks with 100 mL of heavy metal solution. The flasks were placed in a thermostatic shaker and agitated for 150 min at a fixed agitation speed of 700 rpm. Samples were taken periodically for measurement of aqueous phase of heavy metal concentrations. Adsorption isotherms were performed for initial heavy metal concentrations of 250-1,250 ppm. The Zn(II) concentration of the samples were determined by using a Varian Liberty 220 inductive coupled plasma emission spectrometer (ICP-ES). The amount of adsorbed Zn(II) ions (mg metal ions/g biomass) were calculated from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the biosorbent. Adsorption isotherms for zinc(II) ions removal by modified corn cob in terms of Langmuir, Freundlich and Temkin models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of two-parameter isotherm models. Furthermore, the pseudo-first-order and pseudo-second-order models were examined using different temperatures in this paper.

3. Results and discussion

3.1. Effect of parameters on biosorption potential

Fig. 1 (a) illustrates the biosorption of Zn(II) ions by modified corn cob as a function of initial metal ion concentration. This increase continues up to 750 ppm and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the biosorbent samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the modified corn cob at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in the length between 750 and 1,250 ppm. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution. The metal uptake can be attributed to different mechanisms of ion exchange and adsorption processes as it was concerned in much previous work [14],[15].

Experiments conducted with different initial biomass concentrations show that the metal ions uptakes increase with the biosorbent concentration (Fig. 1 (b)). The number of sites available for biosorption depends upon the amount of the biosorbent. The metal ions uptake was found to increase linearly with the increasing concentration of the biosorbent up to the biomass concentration of 3 g/100 mL. Beyond this dosage, the increase in removal efficiency was lower. Increasing the biosorbent dosage caused a wise in the biomass surface area and in the number of potential binding sites [16].

From Fig. 1 (c), the amounts of adsorbed ions onto the modified corn cob increase with an increase in the temperature of heavy metal solution. The maximum adsorption capacities was calculated as 70.20 mg Zn(II) per 1 g biomass for initial concentration of 500 ppm at 70 ^{o}C, showed that this biosorbent was suitable for heavy metals removal from aqueous media. Concerning the effect of temperature on the adsorption process, the metals uptake is favored at higher temperatures, since a higher temperature activates the metal ions for enhancing adsorption at the coordinating sites of the minerals. Also, it is mentioned that cations move faster with increasing temperature. Likely explanation for this is that retarding specific or electrostatic, interactions become weaker and the ions become smaller, because solvation is reduced [17],[18].

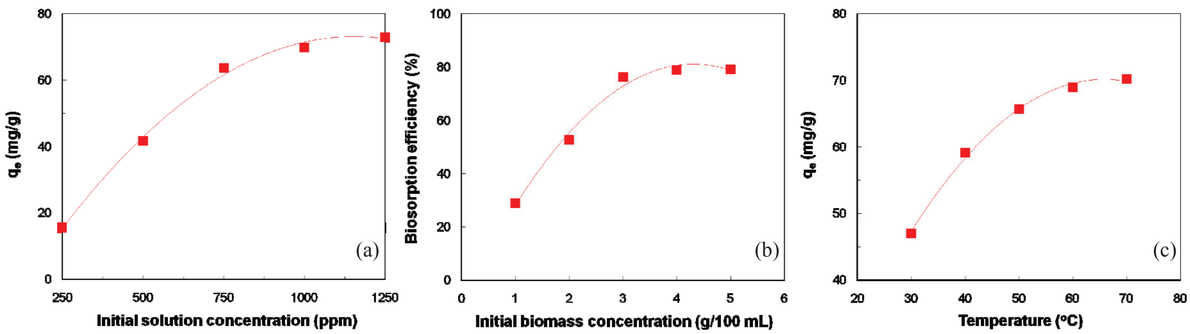

Fig. 1. Effect of (a) solution concentration; (b) biomass concentration; (c) temperature on the biosorption of Zn(II) ions from wastewater

3.2. Equilibrium and kinetic studies of biosorption

The relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by two-parameter isotherm models. The isotherm constants and corresponding correlation coefficients for the adsorption of Zn (II) are presented in Table 1. The correlation coefficients demonstrate that Langmuir, Freundlich and Temkin models adequately fitted the data for biosorption. However, the correlation coefficients (R^2) values are higher in the Freundlich model for zinc adsorption when compared to other models. The Temkin isotherm shows a higher correlation coefficient, which may be due to the linear dependence of heat of adsorption at low or medium coverages. This linearity may be due to repulsion between adsorbate species or to intrinsic surface heterogeneity [13],[19]. The experimental data for heavy metal ions fit well with the linearized Langmuir, Freundlich and Temkin isotherms. R^2 values ranged from 0.9778 to 0.9912 for adsorption of Zn(II). These results indicated that the equilibrium adsorption data of zinc conformed reasonably well to the two-parameter isotherm models equations. q_{eq}, k_1, k_2 and R^2 values at different temperatures are shown in Table 2. The results show that R^2 values for the first-order kinetic model obtained are very low, so the pseudo-first-order model does not support the biosorption kinetics of Zn(II) onto modified corn cob. Analysis indicated that pseudo-second-order kinetics controlled the adsorption rate [20].

Table 1. Isotherm constants for the biosorption of Zn(II) on modified corn cob

Isotherm constants	Langmuir			Freundlich			Temkin		
	K_L	a_L	R^2	K_F	n	R^2	K_{Te}	b	R^2
Zn(II)	14.6041	0.1800	0.9778	3.3447	2.4864	0.9886	4.5540	0.9210	0.9912

Table 2. Kinetic model constants for the biosorption of Zn(II) on modified corn cob

Temperature (K)	pseudo- first-order			pseudo-second-order		
	q_{eq}	k_1	R^2	q_{eq}	k_2	R^2
303	32.68	0.0074	0.7413	45.13	0.0076	0.9960
313	45.67	0.0093	0.6854	60.28	0.0082	0.9987

4. Conclusion

Corn cob is an environmentally friendly potential biosorbent for heavy metals. This work examined the efficiency of this sorbent in removal of Zn(II) ions from aqueous environment. The results indicated that several factors such as initial solution concentration, initial biomass concentration and temperature affect the biosorption process. The experimental data were fitted with the Langmuir, Freundlich and Temkin isotherm and the adsorption process best followed the pseudo-second-order model, which is in agreement with chemical sorption being the rate-controlling step.

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